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ISSN 0543-5846
METABK 48(4) 239-242 (2009)
UDC-UDK 669:66.046.58:532.612=111

STUDY OF SURFACE TENSION OF INORGANIC MELTS BASED ON THEIR CHEMICAL COMPOSITION AND TEMPERATURE

Received – Prispjelo: 2008-09-09
Accepted – Prihvaćeno: 2009-01-10
Original Scientific Paper – Izvorni znanstveni rad

The paper deals with the investigation of selected physical – chemical properties of inorganic melts with respect to behaviour of surfaces. An explorational approach was applied in order to acquire original data enabling extension of the existing databases of material properties. The research itself was realised on a series of samples of oxidic melts obtained by incremental additions of CaO. Temperature was another criterion for observation of changes of properties of investigated systems. The obtained data describing their macroscopic behaviour were then interpreted on the basis of realised X-ray diffraction analyses and published theories on structures of ionic melts. This confrontation made it possible to complete theoretical notions of physical – chemical properties of melts, which worked so far only with homogenous systems.

Key words: surface tension, oxidic melts, slags

Istraživanje površinske napetosti anorganskih talina temeljem njihovog kemijskog sastava i temperature. Rad prikazuje istraživanje određenih fizikalno – kemijskih svojstava anorganskih talina obzirom na ponašanje njihovih površina. Primijenjen je istraživački pristup radi prikupljanja izvornih podataka za proširivanje postojećih datoteka svojstava materijala. Samo istraživanje provedeno je na seriji uzoraka oksidnih talina dobivenih dodavanjem rastućih udjela CaO. Drugi kriterij promatranja promjena eksperimentalnih svojstava bila je temperatura. Prikupljeni podaci o makroskopskom ponašanju potom su interpretirani temeljem analize difrakcijom X –zrakama i dostupnih teorija o strukturama ionskih talina. Ovakav pristup omogućio je upotpunjavanje teorijskih razmatranja fizikalno – kemijskih svojstava talina, koja su dosad bila primjenjiva isključivo za homogene sustave.

Ključne riječi: površinska napetost, oksidne taline, troska

INTRODUCTION

At present scientists lack comprehensive sets of information describing heterogeneous processes at high temperatures, as partial data are obtainable only with difficulties. In spite of that the knowledge of physical – chemical regularities in molten poly-component oxidic systems is essential for many disciplines [1-3]. Although numerous models for calculation of their properties were developed, character of the obtained results is rather only approximate with limited area of application [4]. Many authors have formulated their concept of possible distribution of particles. The "WSM" [5] and Pretnar's theories [6] seem to be fundamental. They assume in the melt associated silicate macro-molecules with different degree of complexity.

Models of Gaskel [7] and Baes [8] further develop theories of occurrence of strings and they are almost inapplicable in practice due to absence of the input data.

Butler [9] has derived on the basis of activity of components in surface and voluminal phase a semi-empiric equation for calculation of the surface tension of binary system. Tanaka [10] has further modified the Butler's equation for molten salts. Authors of the works [11, 12] have modified this model for poly-component oxidic melts. The Choi's model [13] can be applied on ternary systems with limited solubility.

In spite of that none of the existing models can cover the extensive temperature interval of forming of oxidic poly-component melts consisting of melting and dissolution of the input components of heterogeneous mixture accompanied by many chemical reactions. For this reason the presented work deals with experimental study and analysis of surface tension of poly-component slag systems in order to approximate mutual relationships of investigated parameters to chemical and structural changes.

EXPERIMENT

Experimental methods

A sessile drop method was chosen for measurement of surface tension with respect to the character of the measured systems. The principle of this method is based on evaluation of geometric parameters of a droplet lying

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on a non-wettable plate. The values of surface tensions were obtained from the contour of the droplets by mathematical solution based on the Laplace's equation.

Experiment was realised in an enclosed horizontal tubular Tamman's furnace with inert argon atmosphere. Due to oxidic character of investigated systems the plate was made from graphite. The sample was scanned with a 3-chip CCD camera.

Due to occurrence of anomalies during measurement a high-temperature phase diffraction analysis was applied as it enables interpretation of possible phenomena. The measurement itself was made with use of the automatic X-ray diffractometer D 500 made by SIEMENS, which was completed with high-temperature chamber made by PAAR and directionally sensitive detector ELPHYSE.

Experimental material

The initial analysed system, marked in the work as the system A, was a sample of the refining slag with chemical composition specified in Table 1. It is a quasi-quaternary system consisting mostly of the components CaO, Al_2O_3, SiO_2 and MgO. Precise chemical composition was determined by the X-ray fluorescent spectrometry.

Table 1. **Chemical composition of investigated system A**

component	A /wt.%
CaO	45,48
Al_2O_3	41,16
MgO	5,32
SiO_2	5,56
Fe_2O_3	0,68
TiO_2	1,22
K_2O	0,17

Next step was to study the influence of the CaO content on behaviour of the melt. For this purpose series of samples were prepared with incremental increase in CaO always by 3 wt.%. In this manner the samples with concentration interval from 45,48 – 57,48 wt.% CaO were obtained (i.e. with concentrations 48,48; 51,48; 54,48; 57,48 wt.% CaO). Prior to measurement the samples were annealed and moisture was removed from them. They were homogenised by grinding and pressed into the form of a tablet with mass of approx. 1g.

OBTAINED RESULTS

First the temperature dependence of surface tension of the initial system A was determined (Figure 1). The zone of softening of this system falls into the temperature interval 1633-1643 K.

Then the initial mineralogical composition was assessed. The amorphous component represented almost

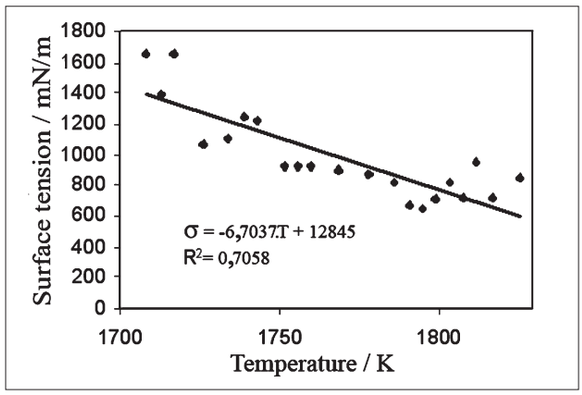

Figure 1. Temperature dependence of surface tension in the system A

half of the content. Calcium aluminium oxide, as well as larnite, akermanite and mayenite were present in greater extent. Phases of portlandite and periclase (Figure 2) were present in smaller extent.

It was established from evaluation of the X-ray diffraction spectra that when the sample was heated to 1573 K all the phases were dissolved and only the phases FeO and MgO were identifiable. When the temperature exceeded 1700 K the whole sample was already liquid. For this reason the obtained values of surface tension can be considered as relevant only above this temperature.

Temperature dependences of surface tension were determined experimentally in all the systems of the concentration series formed by incremental additions of CaO to the original sample A. The obtained results were fitted by linear regression and presented in the form of isotherms (Figure 3).

DISCUSSION OF RESULTS

Interpretation of the obtained results is somewhat problematic due to complexity and chemical diversity of

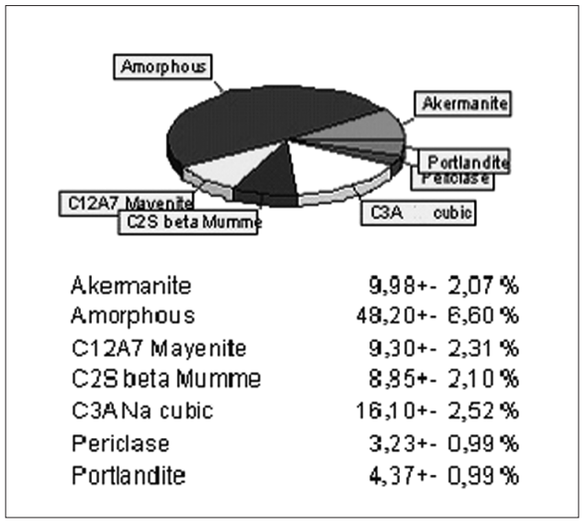

Figure 2. Mineralogical composition of the initial system

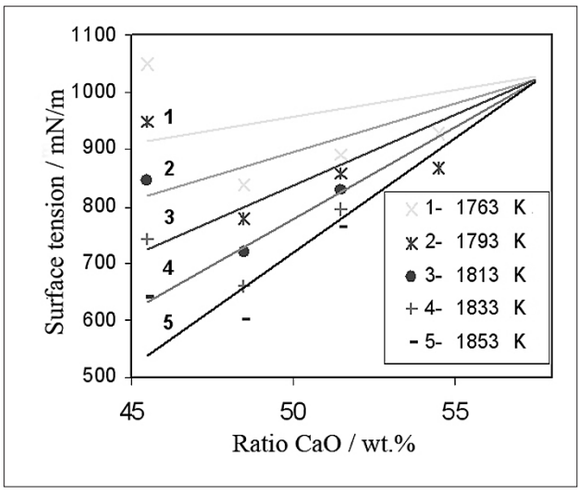

Figure 3. The surface tension dependence on CaO concentration in various temperature

the investigated system. For this reason it is impossible to apply on theoretical calculation of surface properties majority of the existing models working with binary and ternary systems [4 - 10].

Surface tension of slags is influenced by the proper structure of the melt. The obtained values of surface tension are comparatively high in comparison e.g. with silicate melts and Fe_xO melts. This is in accordance with e.g. the work [10], in which it was found that the surface tension increases with decreasing SiO_2, and with increasing CaO and Al_2O_3. Comparatively high measured values of surface tension are related also to very low content of Fe_2O_3. In most steelmaking slags Fe^{3+} will act as a network-breaker [14].

From the viewpoint of older theories, for example according to Daněk [15], who defines on the basis of relation x_{CaO} / x_{MeO} the share of atoms Al^{3+} in related systems, which can participate in formation of poly-anion networks, approximately half of Al^{3+} atoms would be oriented in tetrahedral manner and it would participate in formation of poly-anion networks. Remaining part of aluminium atoms would belong to octahedral coordination and these atoms would behave as structure modifiers. This assumption disagrees slightly with the theory of Nguyen [16], who assumes for the given system tetrahedral coordination in all aluminium atoms. Mills [17] also assumes in his works tetrahedral coordination of aluminium cations and their influence on overall polymerisation of the melt.

It is generally valid that if ions Si^{4+} appear in the melt, they would have a decisive influence on its structure, since silicon is the most electrically negative of all participating elements and it creates together with oxygen stable complexes with firm covalent bond. This assumption is used for explanation of structure of silicate melts and of their influence on surface tension for example by Melamud [14]. It is always necessary to take into account that the system presented in this work contain only very little amount of SiO_2. Formation of more complex ions can occur only within the frame of the ions Al^{3+}, which can possibly with participation of silicon form complex ions of the type $Al_2SiO_7^{4-}$.

Figure 1 shows temperature dependence of surface tension of the initial system. Application of X-ray diffraction analysis established extinction of individual phases below the temperature of 1703 K. For this reason at the temperature slightly above the liquidus there occur anomalies of temperature trends of surface tension and results are not quite reproducible. Above the temperature of 1703 K almost linear drop of suten occurs till the end of measurement due to increase of kinetic energy of particles and weakening of interactions between them.

Analysis of influence of CaO on surface properties (Figure 3) showed that similar trend of development is evident. According to the theory of Nguyen [16] at complete absence of bridging oxygen in the melt the increase of CaO content in the system would cause only small changes of absolute values of surface tension. At the same time CaO has, for example in respect to Al_2O_3, low value of partial molar surface tension. It is therefore possible to expect in a melt with insufficiently formed network structures two contradictory effects at additions of CaO – increase of surface tension due to modification properties of calcium oxide and simultaneously its decrease due to its low partial value.

Assuming of imperfectly formed network structures in the melt the additions of CaO would lead at higher concentrations to decrease of the system surface tension. Modification effect would therefore be to a certain extent compensated by the value of partial molar tension of CaO [18, 12]. Authors Choi and Lee [13] have also confirmed that for a given SiO_2 content, the surface tension was relatively independent on the CaO/Al_2O_3 ratio. It is also necessary to realise that majority of the systems investigated within the frame of this work showed in the presented temperature interval a negative value of the expression ($d\sigma/dT$). These conclusions correspond also with assumptions of the authors investigating the similar systems [19].

CONCLUSIONS

Individual findings can be summarised as follows:

– The established trend of temperature dependence of surface tension of poly-component oxidic system corresponds with generally accepted notions of decrease of surface tension with temperature of melts only in limited temperature interval.
– Phase changes established by X-ray diffraction analysis correspond with anomalies in behaviour of surface properties of melts near the liquidus temperature.

– Increase in CaO content increases within the frame of investigated temperature intervals the values of surface tension at all temperatures.

Authors thank to the Czech Science Foundation projects, Nos. 106/06/1225 and 106/09/0370.

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Note: The responsible for English language is Boris Škandera, Czech Republic